Specific Heat of Electron Gas

Hand waving arguement

specific heat per volume $c_v = \frac{du}{dT}$
where $u = \frac{E}{V}$ is energy per volume

When start at $T=0$ and increase temperature to T, it is only the electrons within k_BT of ε_F that can absorb $\Delta\varepsilon = k_BT$ of energy from the thermal bath. So the change in energy per volume is

$u - u_0 = \Delta u = k_BT \times$ (number of electrons that absorb energy from heat bath per volume)

The ~~mod~~ number of electrons that absorb energy is just the number of electrons with $\Delta\varepsilon = k_BT$ of the Fermi energy. This is $\underset{\uparrow}{g}(\varepsilon_F)\Delta\varepsilon = g(\varepsilon_F)k_BT$

density of electrons per energy per volume

So

$$\Delta u = (k_BT)\, g(\varepsilon_F)\, k_BT = g(\varepsilon_F)(k_BT)^2$$

So $$c_v = \frac{d\Delta u}{dT} = 2g(\varepsilon_F)k_B^2 T \sim T$$

Specific heat of conduction electrons at $T \ll T_F$ is <u>linear</u> in temperature and proportional to the density of states at the Fermi energy $g(\varepsilon_F)$. We will see that many thermodynamic quantities are proportional to $g(\varepsilon_F)$. This is because it is only the electrons close to ε_F that are able to do anything different from the ground state at finite T, (when $T \ll T_F$) and $g(\varepsilon_F)$ gives the density of such electrons.

For the free electron gas we had

$$g(\varepsilon) = \frac{3}{2} \frac{n}{\varepsilon_F} \sqrt{\frac{\varepsilon}{\varepsilon_F}}$$

so $g(\varepsilon_F) = \frac{3}{2} \frac{n}{\varepsilon_F}$

$$\Rightarrow \quad c_v \sim 3n \frac{k_B^2 T}{\varepsilon_F} = 3 n k_B \left(\frac{T}{T_F}\right)$$

Compare this to a classical ideal gas where

$$c_v = \frac{3}{2} n k_B$$

We see that the specific heat of the quantum fermi gas is $\sim (T/T_F) \sim 10^{-2}$ times smaller at room temperature.
Also, whereas the classical c_v is independent of temperature, the quantum c_v is linear in temperature. This difference will help fix some of the problems with the classical Drude model.

A more precise calculation using the Sommerfeld expansion (see Ashcroft + Mermin pgs 45-47, Eq (2-81) or Kittel pgs 142-144) gives the result

$$\boxed{c_v = \frac{\pi^2}{3} g(\varepsilon_F)\, k_B^2\, T}$$

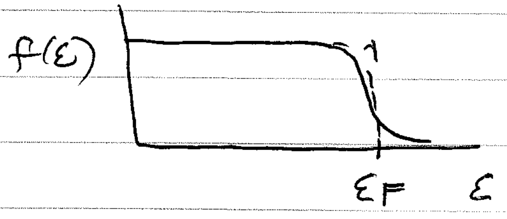
<u>Quick derivation</u> (from Kittel)

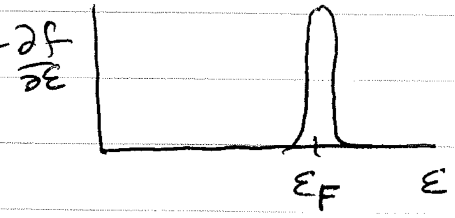
① $u = \int_0^\infty d\varepsilon\, g(\varepsilon)\, \varepsilon\, f(\varepsilon) \Rightarrow \frac{du}{dT} = \int_0^\infty d\varepsilon\, g(\varepsilon)\, \varepsilon\, \frac{\partial f}{\partial T}$

② $n = \int_0^\infty d\varepsilon\, g(\varepsilon) f(\varepsilon) \Rightarrow 0 = \frac{\partial n}{\partial T} = \int d\varepsilon\, g(\varepsilon)\, \frac{\partial f}{\partial T}$

Subtract ε_F times ② from ①

$$c_v = \frac{du}{dT} = \frac{du}{dT} - 0 = \int_0^\infty d\varepsilon\, g(\varepsilon)\, (\varepsilon - \varepsilon_F)\, \frac{\partial f}{\partial T}$$





$\frac{\partial f}{\partial T} \approx 0$ except for energies within k_BT of ε_F

$\Rightarrow$ approx $g(\varepsilon)$ in integral by constant $g(\varepsilon_F)$

$$\frac{\partial u}{\partial T} = g(\varepsilon_F) \int_0^\infty d\varepsilon \, (\varepsilon - \varepsilon_F) \left(\frac{\partial f}{\partial T}\right)$$

$$\frac{\partial f}{\partial T} = \frac{\partial}{\partial T}\left[\frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1}\right] \simeq \left(\frac{\partial f}{\partial x}\right)\left(\frac{\varepsilon - \mu}{k_B T^2}\right)$$

where $x = \left(\frac{\varepsilon - \mu}{k_B T}\right)$. [ignore $\mu(T)$ dependence on T since $\mu \simeq \varepsilon_F$. Corrections give higher order terms]

At low $T \ll T_F$, we can replace $\mu(T) \approx \varepsilon_F$

$$\text{So } \frac{\partial u}{\partial T} = g(\varepsilon_F) \int_{-\infty}^{\infty} d\varepsilon \, \frac{(\varepsilon - \varepsilon_F)^2}{k_B T^2} \left(\frac{-\partial f}{\partial x}\right)$$

$$= g(\varepsilon_F) k_B^2 T \int_{-\infty}^{\infty} dx \, x^2 \left(-\frac{\partial f}{\partial x}\right)$$

$$= g(\varepsilon_F) k_B^2 T \underbrace{\int_{-\infty}^{\infty} dx \, x^2 \frac{e^x}{(e^x+1)^2}}_{=\frac{\pi^2}{3}}$$

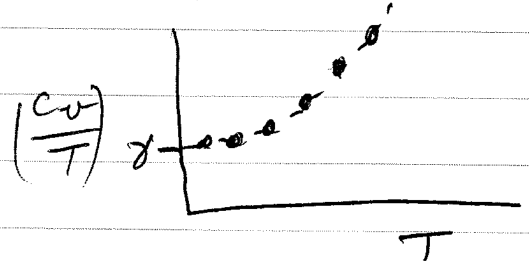
$$\Rightarrow \quad C_v = \frac{\partial u}{\partial T} = \frac{\pi^2}{3} g(\varepsilon_F) k_B^2 T$$

Above is just the contribution to the specific heat of a metal from the conduction electrons. The total specific heat of the metal also includes contributions from vibrations of the ions. This ionic contribution goes like $3n_{ion}k_B$ at high temperatures ($n_{ion} = n/Z$ is ion density; Z = electron valence) but at low T, we will find that due to quantum effects it goes like T^3. So at high $T \sim$ room temp, the ionic contribution to metallic specific heat dominates the electronic part, and we cannot measure the electronic part to test it against theory. But at low T, one can measure c_v and fit it to the form

$$c_v = \gamma T + A T^3$$

where our calculation predicts $\gamma = \overbrace{\frac{\pi^2}{2}\frac{n k_B}{T_F}}^{\text{function of density } n}$

One plots $\frac{c_v}{T} = \gamma + AT^2$ and determines γ by extrapolating to the $T \to 0$ intercept



one finds (see A+M table 2.3)

metal	γ (theory)	γ (expt)	$\left(10^{-4} \frac{\text{cal}}{\text{mole } {}^{\circ}K^2}\right)$
Li	1.8	4.2	
Na	2.6	3.5	
K	4.0	4.7	
Rb	4.6	5.8	
Mn	1.5	40.	
Fe	1.5	12	
Bi	4.3	0.2	

The alkali metals (Li, Na) come out reasonable
The noble metals (Cu, Ag, Au) come out reasonable
Both alkali & noble metals have valence $Z=1$

But there are much bigger discrepencies for

$$\underbrace{\text{Fe, Mn}}_{\substack{\uparrow \\ \sim 10 \text{ times too big}}},\ \underbrace{\text{Bi, Sb}}_{\substack{\uparrow \\ \sim 10 \text{ times too small}}}$$

The difference between γ_{theory} and γ_{expt} is usually due to the difference between the real $g(\varepsilon_F)$ and the free electron approximation for $g(\varepsilon_F)$. This is because the potential energy due to the ions shifts the energy spectrum ε_k from the simple free electron $\hbar^2k^2/2m$,
We can often approx the true ε_k near ε_F as $\hbar^2k^2/2m^*$
where m^* is the effective mass that can be either bigger or smaller than the free electron mass.

Transport Properties of the Sommerfeld Model

We have seen that we ~~must~~ use quantum Fermi-Dirac statistics to describe the thermodynamic behavior of conduction electrons.

What about the equation motion? Semiclassical arguments can be made to show that in many cases it remains OK to use the classical Drude equation of motion. We need to be able to construct electron wave packets which are localized on the desired spatial length scales.

We saw that the typical electron energy is set by the Fermi energy ε_F. Hence the typical momentum is $p \sim p_F$. If we make a wave packet with $\Delta p \ll p_F$ then spread in spatial position is

$$\Delta x \sim \frac{\hbar}{\Delta p} \gg \frac{1}{k_F} \sim r_s$$

So the electron cannot be localized to atomic length scales, but can be localized on the length scales of macroscopically varying electric, magnetic fields or temperature gradients ~ 1000 Å. So OK for motion in EM waves in visible spectrum but not for X-rays ($\lambda_{xray} \sim \text{Å}$).

We also need $\Delta x \ll l$ the mean free path. Classical motion may fail when $l \sim 10\,\text{Å}$.

$l \simeq v\tau$ where $\tau \sim 10^{-14}$ sec and
$v \sim v_F \sim 10^{8}$ cm/sec
so $l \sim 10^{8} \cdot 10^{-14}$ cm $= 10^{-6}$ cm $= 100\,\text{Å}$
so looks ok.

Using Drude ~~of~~ Equation motion + Fermi Dirac Statistics we then have

① dc and ac electric conductivity same as for classical Drude model, since no thermo was involved

② For thermal conductivity we had

$$\kappa = \frac{1}{3} v^2 \tau c_v$$

Now we should use $v \sim v_F$, $v_F^2 = \frac{2\varepsilon_F}{m}$
and $c_v = \frac{\pi^2}{3}\left(\frac{k_B T}{\varepsilon_F}\right) n k_B$

$$\Rightarrow \quad \kappa = \frac{1}{3}\,\frac{2\varepsilon_F}{m}\,\frac{\pi^2}{2}\left(\frac{k_B T}{\varepsilon_F}\right) n k_B\,\tau$$

$$= \frac{\pi^2}{3m}\,\tau\, n k_B^2\, T$$

and Wiedemann - Franz coefficient is

$$\frac{K}{\sigma T} = \frac{\frac{\pi^2}{3m}\tau n k_B^2}{\frac{ne^2\tau}{m}} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.44\times10^{-8} \text{ watt-ohm}/°K^2$$

excellent agreement with experiment

③ Thermopower

$$Q = -\frac{c_v}{3ne} = -\frac{\pi^2}{6}\frac{k_B}{e}\left(\frac{k_BT}{\varepsilon_F}\right)$$

$$= -1.42\left(\frac{k_BT}{\varepsilon_F}\right)\times10^{-4} \text{ volt}/°K$$

more reasonable result than classical value